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manufacture

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ART-UNIT: 175

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ABSTRACT:

A method is provided for making a membrane electrode that employs a composite membrane, which include both a porous membrane and an ion conducting electrolyte, by partially filling a porous membrane with an ion conducting electrolyte to form a partially filled membrane and then compressing the partially filled membrane with electrode so as to remove void volume from the partially filled membrane and embed the electrode in the partially filled membrane. The membrane electrode of this invention is suitable for use in electrochemical devices, including proton exchange membrane fuel cells, electrolyzers, chlor-alkali separation membranes, and the like.

14 Claims, 12 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 10

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Abstract Text - ABTX (1):

A method is provided for making a membrane electrode that employs a composite membrane, which include both a porous membrane and an ion conducting electrolyte, by partially filling a porous membrane with an ion conducting electrolyte to form a partially filled membrane and then compressing the partially filled membrane with electrode so as to remove void volume from the partially filled membrane and embed the electrode in the partially filled membrane. The membrane electrode of this invention is suitable for use in electrochemical devices, including proton exchange membrane fuel cells, electrolyzers, chlor-alkali separation membranes, and the like.

Brief Summary Text - BSTX (6):

In a typical hydrogen/oxygen fuel cell, the ions to be conducted by the membrane are protons. Importantly, ICMs do not conduct electrons/electricity, since this would render the fuel cell useless, and they must be essentially impermeable to fuel gasses, such as hydrogen and oxygen. Any leakage of the gasses employed in the reaction across the MEA results in waste of the reactants and inefficiency of the cell. For that reason, the ion exchange membrane must have or no permeability to the gasses employed in the reaction.

Brief Summary Text - BSTX (12):

Various structures and means have been used to apply or otherwise bring a catalyst in contact with an electrolyte to form electrodes, e.g., cathodes and anodes. These "membrane electrode assemblies" (MEAs) can include: (a) porous metal films or planar distributions of metal or carbon supported catalyst powders deposited on the surface of the ICM; (b) metal grids or meshes deposited on or imbedded in the ICM; or (c) catalytically active nanostructured composite elements embedded in the, surface of the ICM.

Brief Summary Text - BSTX (15):

Briefly, this invention provides a method of making a membrane electrode assembly that comprises a composite membrane, which includes both a porous membrane and an ion conducting electrolyte, by partially filling a porous membrane with an ion conducting electrolyte to form a partially filled membrane and then compressing together the partially filled membrane and electrode so as to remove void volume from the partially filled membrane and embed the electrode in the partially filled membrane. The membrane electrode assembly of this invention is suitable for use in electrochemical devices, including proton exchange membrane fuel cells, electrolyzers, chlor-alkali separation membranes, sensors and the like.

Brief Summary Text - BSTX (19):

In the method of the present invention, a porous membrane is partially filled with an ion conducting electrolyte to form a partially filled membrane. The partially filled membrane is then pressed with electrode so as to embed the electrode in the partially filled membrane. It was found that this pressing step also removed void volume remaining after the filling step, and therefore resulted in a thinner and less porous composite membrane than previously contemplated. In a preferred embodiment, the present invention provides a method for forming a membrane electrode assembly that comprises embedded electrode which may be nanostructured catalyst together with a composite membrane.

Drawing Description Text - DRTX (8):

FIG. 7 is a graph of a polarization curve of voltage versus current produced by two fuel cell assemblies of the present invention.

Drawing Description Text - DRTX (9):

FIG. 8 is a graph of a polarization curve of voltage versus current produced by a fuel cell assembly of the present invention.

Detailed Description Text - DETX (2):

In the method of the present invention, a porous membrane is partially filled with an ion conducting electrolyte to form a partially filled composite membrane. The partially filled membrane is then compressed with electrode so as to further exclude void volume from the membrane and embed the electrode in the membrane.

Detailed Description Text - DETX (4):

More preferably, porous membranes of the invention comprise microporous films prepared by thermally-induced phase separation (TIPS) methods, as described in, e.g., U.S. Pat. Nos. 4,539,256, 4,726,989, 4,867,881, 5,120,594 and 5,260,360, the teachings of which are incorporated herein by reference. TIPS films exhibit a multiplicity of spaced, randomly dispersed, equiaxed, nonuniform shaped of a thermoplastic polymer in the form of a film, membrane, or sheet material. Micropores defined by the preferably are of sufficient size to allow ICMs to be incorporated therein. FIGS. 3 and 9 are scanning electron micrographs at 2000.times. and 1000.times. magnification, respectively, of the porous surfaces of two such TIPS membranes.

Detailed Description Text - DETX (5):

Polymers suitable for preparing films by the TIPS process include thermoplastic polymers, thermosensitive polymers, and mixtures of these polymers, so long as the mixed polymers are compatible. Thermosensitive polymers such as molecular weight (UHMWPE) cannot be melt-processed directly but can be melt-processed in the presence of a diluent that lowers the viscosity thereof sufficiently for melt processing.

Detailed Description Text - DETX (6):

Suitable polymers include, for example, crystallizable vinyl polymers, condensation polymers, and oxidation polymers. Representative crystallizable vinyl polymers include, for example, polypropylene, polybutadiene, polyacrylates such as poly(methyl methacrylate), fluorine-containing polymers such as poly(vinylidene fluoride), and the like.

Useful condensation polymers include, for example, polyesters, such as poly(ethylene terephthalate) and poly(butylene terephthalate), polyamides, including many members of the Nylon.TM. family, polycarbonates, and polysulfones. Useful oxidation polymers include, for example, poly(phenylene) and poly(ether ketone). Blends of polymers and copolymers may also be useful in the invention. Preferred polymers for use as reinforcing membranes of the invention include crystallizable polymers, such as polyolefins and fluorine-containing polymers, because of their resistance to hydrolysis and oxidation. Preferred polyolefins include polypropylene, ethylene-propylene copolymers, and poly(vinylidene fluoride).

Detailed Description Text - DETX (8):

Ion conductive materials useful in the invention can be complexes of an alkalai metal or alkalai earth metal salt or a protonic acid with one or more polar polymers such as a polyether, polyester, or polyimide, or complexes of an alkalai metal or alkalai earth metal salt or a protonic acid with a network or crosslinked polymer containing the above polar polymer as a segment. Useful polyethers include: polyoxyalkylenes, such as glycol, glycol monoether, glycol diether, polypropylene glycol, polypropylene glycol monoether, and polypropylene glycol diether; copolymers of these polyethers, such as poly(oxyethylene-co-oxypropylene) glycol, poly(oxyethylene-co-oxypropylene) glycol monoether, and poly(oxyethylene-co-oxypropylene) glycol diether; condensation products of ethylenediamine with the above polyoxyalkylenes; esters, such as phosphoric acid esters, aliphatic carboxylic acid esters or aromatic carboxylic acid esters of the above polyoxyalkylenes. Copolymers of, e.g., glycol with dialky siloxanes, glycol with maleic anhydride, or glycol monoethyl ether with methacrylic acid are known in the art to exhibit sufficient ionic conductivity to be useful in an ICM of the invention. Useful complex-forming reagents can include alkalai metal salts, alkalai metal earth salts, and protonic acids and protonic acid salts. Counterions useful in the above salts can be halogen ion, perchloric ion, thiocyanate ion, trifluoromethane sulfonic ion, borofluoric ion, and the like. Representative examples of such salts include, but are not limited to, lithium fluoride, sodium iodide, lithium iodide, lithium perchlorate, sodium thiocyanate, lithium trifluoromethane sulfonate, lithium borofluoride, lithium hexafluorophosphate, phosphoric acid, sulfuric acid, trifluoromethane sulfonic acid, tetrafluoroethylene sulfonic acid, hexafluorobutane sulfonic acid, and the like.

Detailed Description Text - DETX (12):

Any suitable procedure may be used to partially fill the porous membrane

with the electrolyte. In the "multiple dipping" approach, illustrated in the Examples, the porous membrane is immersed in relatively concentration electrolyte solution for short times, dried, and the process repeated multiple times. The dipping may be repeated until the weight of the membrane approaches a steady state as no further electrolyte is incorporated. Preferably, the dipping is repeated until at least this point, but may be terminated before this point. Any concentration of electrolyte solution may be used, however, very concentrations may require increased dipping repetitions or may result in lower loading of electrolyte. A solution of about 5 wt % is preferred. The membrane may be dried by any means, preferably at elevated temperature such as in an air oven. Drying temperature is preferably between 40.degree. C. and 60.degree. C. Without being limited to any one theory, it is proposed that the adsorption of the electrolyte polymer onto the porous matrix fibrils occurs primarily as the concentration of the solution increases during the solvent evaporation stage, so increasing the number of such events will enhance filling.

Detailed Description Text - DETX (13):

In the "long soak" approach, illustrated in the Examples, the porous membrane is immersed in the electrolyte solution for prolonged periods, preferably exceeding 20 minutes, then dried. Any concentration of electrolyte solution may be used, however, very concentrations may require increased soaking time or may result in lower loading of electrolyte. A solution of about 5 wt % is preferred. The membrane may be dried by any means, preferably at elevated temperature such as in an air oven. Drying temperature is preferably between 40.degree. C. and 60.degree. C.

Detailed Description Text - DETX (15):

In the "hydraulic press" approach, illustrated in the Examples, a room temperature mechanical press is used to force concentration viscous electrolyte solutions through the porous membrane. Preferably, the membrane material is sandwiched between impermeable film layers having mask holes cut in the area to be filled with electrolyte. The mask layers may be prepared from terephthalate (PET) film, preferably about 100 micrometers thick. The electrolyte solution is added dropwise to the membrane surface. Additional layers or shims may be added before the membrane is placed in the press. The pressure used may be up to 2 tons/cm.^{sup.2}, preferably between 0.1-1.0 tons/cm.^{sup.2}, and more preferably 0.4-0.6 tons/cm.^{sup.2}. Any means of applying pressure may be employed, including nip rollers and flat bed presses. A continuous process is preferred. Force is applied for as long as necessary to partially fill the membrane, typically between 1 second and 10 minutes. After pressing, any excess solution is wiped off the surface of the membrane

and the membrane is dried. The membrane may be dried by any means, preferably at elevated temperature such as in an air oven. Drying temperature is preferably between 40.degree. C. and 60.degree. C.

Detailed Description Text - DETX (18):

The amount of electrolyte solution used in the filling process should be sufficient to achieve the degree of filling desired but is preferably in excess of that which would theoretically fill the membrane. The amount of electrolyte imbibed in the pores or adsorbed on the fibrils of the membrane after the partial filling should be sufficient to fill between 10% and 90% of the available pore volume. Preferably, more than 15% of the available pore volume is filled. Most preferably, between 35% and 65% of the available pore volume is filled. The electrolyte may be present as a coating on the structural fibrils of the porous membrane or it may wet out the membrane, filling the entire cross section of some pores. The increase in ρ of the membrane after partial filling should be at least 0.01 g/cm³ but is preferably at least 0.1 g/cm³ but less than 1.2 g/cm³.

Detailed Description Text - DETX (19):

Any suitable electrode may be used. At least a portion of the surface of suitable electrode is composed of a catalytic material. Preferably, nanostructured elements are used, as described below. However, other electrode may be used, including metal fines or metal-coated support such as carbon. The catalytic material should be appropriate to the intended use of the MEA. Preferably the catalytic material is a Group VII metal or an alloy thereof and most preferably Pt or an alloy thereof.

Detailed Description Text - DETX (20):

Nanostructured elements suitable for use in the present invention may comprise metal-coated whiskers of organic pigment, most preferably C.I. PIGMENT RED 149 (perylene red). The crystalline whiskers have substantially uniform but not identical cross-sections, and length-to-width ratios. The nanostructured whiskers are conformally coated with materials suitable for catalysis, and which endow the whiskers with a fine nanoscopic surface structure capable of acting as multiple catalytic sites.

Detailed Description Text - DETX (24):

A layer of whiskers can be deposited on a substrate of any desired size by a totally dry process, and conveniently and rapidly patterned using, for example, resolution (dry) laser ablation means.

Detailed Description Text - DETX (28):

Preferably, the whiskers have an areal number in the range from about $10^{0.7}$ to about $10^{1.1}$ whiskers per square centimeter. More preferably, the whiskers have an areal in the range from about $10^{0.8}$ to about $10^{1.0}$ whiskers per square centimeter.

Detailed Description Text - DETX (30):

Materials useful as a substrate include those which maintain their integrity at the temperature and vacuum imposed upon them during the vapor deposition and annealing steps. The substrate can be flexible or rigid, planar or non-planar, convex, concave, textured, or combinations thereof. Preferred substrate materials include organic materials and inorganic materials (including, for example, glasses, ceramics, metals, and semiconductors). The preferred inorganic substrate material is glass or metal. The preferred organic substrate material is a polyimide. Representative organic substrates include those that are stable at the annealing temperature, for example, polymers such as polyimide film (commercially available, for example, under the trade designation "KAPTON" from DuPont Electronics, Wilmington, Del.), temperature stable polyimides, polyesters, polyamids, and polyaramids. Metals useful as substrates include, for example, aluminum, cobalt, copper, molybdenum, nickel, platinum, tantalum, or combination thereof. Ceramics useful as a substrate material include, for example, metal or non-metal such as alumina and silica. A useful inorganic nonmetal is silicon.

Detailed Description Text - DETX (32):

Useful organic materials for producing whiskers by, for example, coating followed by plasma etching, can include for example, polymers and prepolymers thereof (e.g., thermoplastic polymers such as, for example, alkyds, melamines, urea formaldehydes, diallyl phthalates, epoxies, phenolics, polyesters, and silicones; thermoset polymers, such as acrylonitrile-butadiene-styrenes, acetals, acrylics, cellulose, chlorinated polyethers, ethylene-vinyl acetates, fluorocarbons, ionomers, nylons, parylenes, phenoxies, polyallomers, polyethylenes, polypropylenes, polyamide-imides, polyimides, polycarbonates, polyesters, polystyrenes, polysulfones; and vinyls); and organometallics (e.g., bis(η^5 -cyclopentadienyl)iron (II), iron pentacarbonyl, ruthenium pentacarbonyl, osmium pentacarbonyl, chromium hexacarbonyl, molybdenum hexacarbonyl, tungsten hexacarbonyl, and tris(triphenylphosphine) rhodium chloride).

Detailed Description Text - DETX (33):

Preferably, the chemical composition of the organic-based whisker layer will be the same as that of the starting organic material. Preferred organic

materials useful in preparing the whisker layer include, for example, planar molecules comprising chains or rings over which π -electron is extensively delocalized. These organic materials generally crystallize in a herringbone configuration. Preferred organic materials can be broadly classified as polynuclear aromatic hydrocarbons and heterocyclic aromatic compounds.

Detailed Description Text - DETX (38):

Orientation of the whiskers can be affected by the substrate temperature, the deposition rate, and angle of incidence during deposition of the organic layer. If the temperature of the substrate during deposition of the organic material is sufficiently (i.e., above a critical substrate temperature which has been associated in the art with a value one-third the boiling point (K) of the organic material), the deposited organic material will form randomly oriented whiskers either as deposited or when subsequently annealed. If the temperature of the substrate during deposition is relatively (i.e., below the critical substrate temperature), the deposited organic material tends to form uniformly oriented whiskers when annealed. For example, if uniformly oriented whiskers comprising perylene red are desired, the temperature of the substrate during the deposition of the perylene red is preferably about 0 to about 30.degree. C. Certain subsequent conformal coating processes, such as DC magnetron sputtering and cathodic arc vacuum processes, can produce curvilinear whiskers.

Detailed Description Text - DETX (39):

There can be an optimum maximum annealing temperature for different film thicknesses in order to fully convert the deposited layer to whiskers. When fully converted, the major dimension of each whisker is directly proportional to the thickness of the initially deposited organic layer. Since the whiskers are discrete, are separated by distances on the order of their cross-sectional dimensions, and preferably have uniform cross-sectional dimensions, and all the original organic film material is converted to whiskers, conservation of mass implies that the lengths of the whiskers will be proportional to the thickness of the layer initially deposited. Due to this relationship of the original organic layer thickness to the lengths of the whiskers, and the independence of cross-sectional dimensions from length, the lengths and aspect ratios of the whiskers can be varied independently of their cross-sectional dimensions and areal . For example, it has been found that the length of whiskers are approximately 10-15 times the thickness of the vapor deposited perylene red layer, when the thickness ranges from about 0.05 to about 0.2 micrometer. The surface area of the whisker layer (i.e., the sum of the surface areas of the individual whiskers) is much greater than that of the organic layer initially

deposited on the substrate. Preferably, thickness of the initially deposited layer is in the range from about 0.03 to about 0.25 micrometer.

Detailed Description Text - DETX (42):

In the annealing step, the substrate having an organic layer coated thereon is heated in a vacuum for a time and at a temperature sufficient for the coated organic layer to undergo a physical change, wherein the organic layer grows to form a whisker layer comprising a dense array of discrete, oriented monocrystalline or polycrystalline whiskers. Uniform orientation of the whiskers is an inherent consequence of the annealing process when the substrate temperature during deposition is sufficiently . Exposure of the coated substrate to the atmosphere prior to the annealing step is not observed to be detrimental to subsequent whisker formation.

Detailed Description Text - DETX (48):

Useful inorganic materials for producing whiskers include, for example, carbon, diamond-like carbon, ceramics (e.g., metal or non-metal such as alumina, silica, iron and copper ; metal or non-metal nitrides such as silicon nitride and titanium nitride; and metal or non-metal carbides such as silicon carbide; metal or non-metal borides such as titanium boride); metal or non-metal sulfides such as cadmium sulfide and zinc sulfide; metal silicides such as magnesium silicide, calcium suicide, and iron suicide; metals (e.g., noble metals such as gold, silver, platinum, osmium, iridium, palladium, ruthenium, rhodium, and combinations thereof; transition metals such as scandium, vanadium, chromium, manganese, cobalt, nickel, copper, zirconium, and combinations thereof; melting metals such as bismuth, lead, indium, antimony, tin, zinc, and aluminum; refractory metals such as tungsten, rhenium, tantalum, molybdenum, and combinations thereof); and semiconductor materials (e.g., diamond, germanium, selenium, arsenic, silicon, tellurium, gallium arsenide, gallium antimonide, gallium phosphide, aluminum antimonide, indium antimonide, indium tin zinc antimonide, indium phosphide, aluminum gallium arsenide, zinc telluride, and combinations thereof).

Detailed Description Text - DETX (51):

Preferably, the one or more layers of conformal coating material, if applied, serve as a functional layer imparting desirable catalytic properties, as well as electrical conductivity and mechanical properties (e.g., strengthens and/or protects the whiskers comprising the whisker layer), and vapor pressure properties.

Detailed Description Text - DETX (53):

The preferred thickness of the conformal coating is typically in the range

from about 0.2 to about 50 nm. The conformal coating may be deposited onto the whisker layer using conventional techniques, including, for example, those disclosed in U.S. Pat. Nos. 4,812,352 and 5,039,561, the disclosures of which are incorporated herein by reference. Any method that avoids disturbance of the whiskers by mechanical forces can be used to deposit the conformal coating. Suitable methods include, for example, vapor phase deposition (e.g., vacuum evaporation, sputter coating, and chemical vapor deposition) solution coating or dispersion coating (e.g., (lip coating, spray coating, spin coating, pour coating (i.e., pouring a liquid over a surface and allowing the liquid to flow over the whisker layer, followed by solvent removal)), immersion coating (i.e., immersing the whisker layer in a solution for a time sufficient to allow the layer to adsorb molecules from the solution, or colloids or other from a dispersion), electroplating and electrodeless plating. More preferably, the conformal coating is deposited by vapor phase deposition methods, such as, for example, ion sputter deposition, cathodic arc deposition, vapor condensation, vacuum sublimation, physical vapor transport, chemical vapor transport, and metalorganic chemical vapor deposition. Preferably, the conformal coating material is a catalytic metal or metal alloy.

Detailed Description Text - DETX (55):

The electrode can be embedded in the partially filled membrane by applying heat and mechanical pressure and subsequently removing the original substrate supporting the . Any suitable source of pressure may be employed. A hydraulic press is preferably employed. Alternately, pressure may be applied by one or a series of nip rollers. This process is also adaptable to a continuous process, using either a flat bed press in a repeating operation or rollers in a continuing operation. Shims, spacers, and other intermediate mechanical devices may be employed. The electrode are preferably supported on a substrate which is applied to the membrane surface, such that the contact the membrane surface. The substrate is removed after pressing, leaving the electrode embedded in the membrane. Alternately, the electrode may be applied directly to the membrane surface, free of any substrate and without inclusion of any additional ionomer, and then pressed into the surface. In one embodiment, a partially filled membrane disk may be placed between two sheets of polyimide-supported nanostructured films of nanostructured elements which are placed against the partially filled membrane. Additional layers of uncoated polyimide and PTFE sheets are further layered on either side of the sandwich for uniform distribution of pressure, and finally a pair of stainless steel shims is placed outside of this assembly.

Detailed Description Text - DETX (56):

The pressure, temperature and duration of pressing may be any combination sufficient to exclude void volume from the membrane and embed the electrode in the membrane. The optimum conditions depend on the properties of the porous membrane. Preferably, a pressure of between 0.05 and 10 tons/cm.² is used and more preferably a pressure of between 0.1 and 1.0 ton/cm.². Most preferably, a pressure of between 0.10 and 0.20 ton/cm.² is used. Preferably the press temperature is between 20.degree. C. and 300.degree. C., and most preferably between 80.degree. C. and 250.degree. C. The pressing time is preferably greater than one second and most preferably about one minute. After loading into the press, the MEA components may be allowed to equilibrate to the press temperature, at or no pressure, prior to pressing. Alternately, the MEA components may be preheated in an oven or other apparatus adapted for the purpose. Preferably the MEA components are preheated for 1-10 minutes before pressing. The MEA may be cooled before or after removal from the press. The platens of the press may be water cooled or cooled by any other suitable means. Preferably, the MEA is cooled for 1-10 minutes while still under pressure in the press.

Detailed Description Text - DETX (62):

Examples 1-19, below, demonstrate partial filling of various porous polymer membranes with various ion conducting electrolytes by several different methods. Examples 20-25, following, demonstrate partial filling of the membranes followed by pressing of the partially filled membranes with electrode

Detailed Description Text - DETX (68):

The fourth membrane, Poreflon.TM., is an expanded (PTFE) produced by Sumitomo Electric Industries, Inc., Tokyo, Japan, which has a Gurley number of 17.5.+-.0.5 seconds/100 cc.

Detailed Description Text - DETX (75):

Examples 1 and 2 illustrate partial filling of the porous membranes with electrolyte using a multiple dipping and drying process. In this approach the porous membrane was immersed in concentration electrolyte solution for short times, dried in an air oven, and the process repeated multiple times, with measurements of the mass loading increase in between.

Detailed Description Text - DETX (77):

The average overall mass increase for the 16 dip/dry cycles is about 20 mg, or 1.75 mg/cm.², or 0.61 g/cm.³. The of the Nafion 1100 electrolyte is approximately 2 g/cm.³, based on the of Nafion 117, (1.97 g/cm.³) which is the polymeric electrolyte material of Nafion 1100

out of solution. The increase of 0.61 g/cm^3 corresponds to filling about 30% of the volume of the membrane. Hence, the original void volume of the membrane, 58%, was approximately half filled by the multiple dipping/drying procedure.

Detailed Description Text - DETX (79):

In Example 2, the multiple dipping and drying procedure of Example 1 was repeated with three sample discs of the TIPS membrane C medium. The number of cycles was eleven. The immersion times varied from 4 minutes to 20 minutes and drying times from 18 minutes to 90 minutes. FIG. 2 summarizes the mass changes after each cycle. Again, the measurements indicate that the mass increases for all three samples were similar, that the length of soaking time does not appear to be a significant parameter and that the use of fresh solutions does not appear to have a significant effect. The mass increase is similar for all three samples and appears to level off after the 4th cycle. The average overall mass increase is about 12 mg, or 1 mg/cm^2 , or 0.15 g/cm^3 . The TIPS membrane C medium has a smaller pore size and void volume (44%) than the TIPS membrane B medium which may account for the larger increase in of the latter medium in Ex. 1. The maximum possible increase is calculated to be 0.88 g/cm^3 of Nafion in the TIPS membrane C medium. The increase of 0.15 g/cm^3 corresponds to filling about 7.5% of the volume of the membrane. Approximately a sixth of the original void volume of the membrane, 44%, was filled by the multiple dipping/drying procedure.

Detailed Description Text - DETX (82):

In Example 3, two 3.15 cm diameter discs of TIPS membrane B were filled by soaking in 5 wt % Nafion solution for 30 minutes, then dried in an air oven at 50.degree. C. for 50 minutes. The increases were 0.31 g/cm^3 and 0.26 g/cm^3 respectively, averaging 0.29 g/cm^3 .

Detailed Description Text - DETX (83):

In Example 4, a 3.81 cm diameter disc of TIPS membrane B was soaked for 5 hours in a 5 wt % solution. The container was not covered, so that the concentration could increase with time. After drying in an air oven for 45 minutes at about 50.degree. C., the increase was 0.44 g/cm^3 .

Detailed Description Text - DETX (84):

In Example 5, two, 2.5 cm diameter discs of TIPS membrane A were soaked in 20 wt % p-STSI in DI water for 20 minutes. The excess was allowed to drain off and the discs were dried overnight. For both samples, the increase was 0.16 g/cm^3 .

Detailed Description Text - DETX (86):

Examples 6-12 illustrate partial filling of the porous membranes with electrolyte by use of a vacuum procedure. In this approach a small vacuum is applied to the underside of the porous membrane supported on a flask support, to force various electrolyte concentrations through the membrane.

Detailed Description Text - DETX (87):

In Examples 6-8 portions of the 5 wt % Nafion solution were dried down to prepare 10 and 20 wt % solutions. For each solution, single discs of TIPS membrane A, each 3.81 cm diameter, were placed over the holes in the flat bottom of a Coors D37 ceramic funnel inserted in the top of a 250 ml vacuum flask, connected via a rubber hose to a Venturi air device, Varian model 952-5096 (sold by Varian, Lexington, Mass.) to provide suction. Then 0.5 ml of solution was spread over the top of the membrane and vacuum was applied to pull solution through the membrane. For the most viscous solution, not all solution passed through but remained on the surface of the membrane. The samples were dried for 35 minutes at about 50.degree. C. and weighed. The increase in mass due to electrolyte uptake was observed to increase monotonically with solution concentration from 0.20 g/cm.³ at 5 wt % to 0.36 g/cm.³ at 10 wt % to 0.71 g/cm.³ at 20 wt %. Since any excess left on the surface was not removed for the 20 wt % sample, part of the increase is due to a dried film left covering the surface.

Detailed Description Text - DETX (88):

In Example 9, the TIPS membrane B was filled with Nafion 5 wt % solution in the same apparatus described in Ex. 6. Sample diameters were 3.15 cm. 15 drops of solution were added to the first discs. The solution was allowed to wet the TIPS for 2 minutes, then vacuum was applied for 10 seconds. For the second disc, 17 drops were applied for 3 minutes before vacuum was applied for 50 seconds. After drying the increases were measured to be 0.26 g/cm.³ and 0.35 g/cm.³ respectively.

Detailed Description Text - DETX (89):

In Example 10, two 3.81 cm diameter discs of TIPS membrane C were vacuum loaded with 5 wt % Nafion solution. 15 drops were applied to each surface, allowed to wet for one minute, then vacuum applied for 17 seconds in one case and 50 seconds in the second sample. The samples were dried at 50.degree. C. for 25 minutes. The increases were 0.06 g/cm.³ and 0.054 g/cm.³ respectively.

Detailed Description Text - DETX (90):

In Example 11, three discs, each 3.51 cm diameter, of the TIPS membrane A were partially filled with Nafion using 5 wt % solutions and the vacuum pull through method of Ex. 6. For the first disc, a total of 1 ml of solution was passed through, in two 15 drop lots. For the second 2 ml of solution was passed through and for the third, 3 ml was used. After drying the respective increases were 0.298 g/cm³, 0.301 g/cm³ and 0.303 g/cm³. Example 11 demonstrates that the increase in observed using the vacuum method, and hence the amount of ionomer adsorbed, becomes independent of the total volume of electrolyte solution passed through the membrane.

Detailed Description Text - DETX (91):

In Example 12, two 2.5 cm discs of TIPS membrane A were filled with p-STSI from a 20 wt % solution using the same procedure as in Example 6. Six drops of solution were added to the surface and vacuum applied for 2 minutes. After drying, the change in was 0.17 g/cm³ and 0.13 g/cm³, averaging 0.15 g/cm³.

Detailed Description Text - DETX (93):

Examples 13-19 illustrate partial filling of the porous membranes with electrolyte using positive pressure provided by a hydraulic press. In the hydraulic press approach, a room temperature mechanical press is used to hydraulically force concentration (viscous) electrolyte solutions through the porous membrane.

Detailed Description Text - DETX (94):

In the following Examples, two pieces of 100 micrometer thick terephthalate (PET) film were prepared as masks by cutting 3.7 cm diameter holes in their centers. The porous membrane material was sandwiched between the two PET masks. This sandwich was further sandwiched between two sheets of 0.025 cm thick PTFE, after applying the electrolyte solution into the volume (about 0.1 ml) defined by the holes in the PET mask. This sandwich was placed between stainless steel shim stock. The entire assembly was placed between the platens of a hydraulic press (manufactured by Fred S. Carver, Inc., Wabash, Ind.) and a force of 3.2 tons applied for 3-5 minutes at room temperature. After pressing, excess solution was wiped off the surface of the membrane and the latter dried in an air oven at about 48.degree. C. for 12 minutes. A disc of measured diameter was die cut from the center of the partially filled membrane sample and its mass loading of electrolyte gravimetrically determined.

Detailed Description Text - DETX (95):

In Example 13, two samples of TIPS membrane B were filled with Nafion using a 5 wt % solution and the procedure described above and 3.15 cm diameter discs

were die cut from the resulting membrane. The increases after drying were 0.11 g/cm.sup.3 and 0.076 g/cm.sup.3, averaging 0.093 g/cm.sup.3.

Detailed Description Text - DETX (96):

In Example 14, two samples of the TIPS membrane C were filled with Nafion using a 5 wt % solution and the same procedure as in Ex. 13 and 3.81 cm diameter discs were die cut from the resulting membrane. The increases after drying were 0.037 g/cm.sup.3 and 0.045 g/cm.sup.3, averaging 0.041 g/cm.sup.3.

Detailed Description Text - DETX (97):

In Example 15, the hydraulic press method described in Example 13 was used to fill 3 samples of TIPS membrane B with p-STSI from 20 wt % solutions in 70/30 methanol and water. Three to four drops of solution were used for each side, pressed for 3 minutes at 3 tons, then dried 20 minutes at about 50.degree. C. after wiping the excess electrolyte off the surface. Three 3.25 cm diameter discs were cut from the resulting membrane; The increases were 0.049 g/cm.sup.3, 0.014 g/cm.sup.3 and 0.060 g/cm.sup.3 for an average increase of 0.041 g/cm.sup.3.

Detailed Description Text - DETX (98):

In Example 16, the procedure of Example 15 was repeated with two more samples, using 4 drops on each side from a 20 wt % solution of p-STSI in water only. The excess was wiped off and the samples dried at 55-60.degree. C. for 23 minutes, and 3.81 cm diameter disks were cut from the resulting membranes. The increase were 0.028 g/cm.sup.3 and 0.19 g/cm.sup.3 for an average increase of 0.11 g/cm.sup.3.

Detailed Description Text - DETX (99):

In Examples 17 and 18, the procedures used in Examples 15 and 16 were repeated using, three TIPS membrane C sample discs with 20 wt % solution of p-STSI in 70/30 MeOH/H₂O, for 17 and two sample discs with p-STSI in pure water, for 18. The increases of the first three discs were 0.098 g/cm.sup.3, 0.091 g/cm.sup.3 and 0.149 g/cm.sup.3 averaging 0.113 g/cm.sup.3. The increases of the next two were 0.25 g/cm.sup.3 and 0.088 g/cm.sup.3 averaging 0.17 g/cm.sup.3.

Detailed Description Text - DETX (100):

In Example 19, a 3.85 cm diameter disc of 50 micrometer thick Poreflon.TM. was filled using the procedure of Ex. 13. The porosity of the as received Poreflon was characterized by Gurley measurements and found to be 17.5.+-.0.5 seconds/100 cc. Fifteen drops of a 4 wt % solution of Nafion 1100 was added to

one side of the membrane (in the volume defined by the 100 micrometer thick PET mask aperture) and pressed at 2 tons for 4 minutes at room temperature. The excess Nafion was wiped off and the membrane dried at 49.degree. C. for 15 minutes. The increase was 0.22 g/cm.sup.3. The Gurley number of the filled sample was measured to be over 900 seconds/4 cc, corresponding to 22,500 seconds /100 cc.

Detailed Description Text - DETX (101):

Summary of Increase Data

Detailed Description Text - DETX (102):

Examples 1-19 demonstrate the increase due to electrolyte incorporation by the various porous membranes for four filling procedures. Table I, below, summarizes the average results for Examples (including Example 20, below) that used Nafion electrolyte with four different porous membranes and four different methods. Table II, below, summarizes the average results for Examples (including Example 24, below) that used pSTSI electrolyte with three different porous membranes and three different methods.

Detailed Description Text - DETX (104):

Examples 20-25, following, demonstrate partial filling of the membranes followed by pressing of the partially filled membranes with electrode to form membrane electrodes. The electrode used in Examples 20-25 are nanostructured catalyst consisting of catalyst materials, e.g. Pt, conformally coated onto nanometer sized whisker-like supports, as described above and in U.S. Pat. No. 5,338,430 and other patents referenced therein, incorporated herein by reference. The whiskers used herein were produced by vacuum annealing thin films (about 1000-1500 Angstroms) of perylene red (PR149, described above) previously vacuum coated onto substrates such as polyimide. The whisker-like supports, with lengths of about 1-2 micrometers, were grown with uniform cross-sectional dimensions of about 30-60 nanometers, end-oriented on a substrate to form a dense film of closely spaced supports (about 30-40 per square micrometer) for transfer into the surface of a polymer electrolyte to form the catalyst electrode, as described below. The nanostructured catalyst electrode has a very surface area which is readily accessible to fuel and oxidant gases.

Detailed Description Text - DETX (108):

Next, a three layer membrane electrode assembly, comprising an electrode layer, an ICM, and a second electrode layer, was formed by using heat and pressure to transfer nanostructured electrode from a polyimide substrates into both surfaces of the partially filled membrane. The filled

membrane disc was placed between two sheets of polyimide-supported nanostructured films of nanostructured elements. These elements, which were PR149 whiskers coated with a mass equivalent layer thickness of first 3000 Angstroms of Ni and secondly, 1000 Angstroms of Pt, were placed against the partially filled membrane. Additional layers of uncoated polyimide and PTFE sheets were further layered on either side of the sandwich for uniform distribution of pressure, and finally a pair of stainless steel shims were placed outside of this assembly. The assembly was placed between the heated platens of a mechanical press (Carver 6" press) at pressure, allowed to equilibrate to 99.degree. C. for several minutes, pressed at 15.1 MPa (0.17 tons/cm.sup.2) for 90 seconds, left under pressure while the platens were water cooled for several minutes, then removed. The original polyimide substrates were then peeled away from the membrane. The transfer of catalyst was complete and very uniform.

Detailed Description Text - DETX (111):

FIG. 5 is a scanning electron micrograph taken at 5000.times. of one of the electrode sides showing the electrode embedded in the membrane. The fractured edge of the membrane shows some evidence of the fibril nature of the original polypropylene matrix.

Detailed Description Text - DETX (112):

For comparison., a portion of the membrane that was not filled with Nafion was impregnated with electrode . FIG. 6 is a scanning electron micrograph taken at 4000.times. showing that the thickness of this portion was reduced to about 15 micrometers, or about 1/6.sup.th the original thickness. In contrast, the membrane was only compressed to about 1/3.sup.rd the original thickness after the partial filling step.

Detailed Description Text - DETX (115):

An MEA was formed using nanostructured films composed of electrode supported on a polyimide substrate. The nanostructured electrode used in Example 21 were supported on a polyimide substrate, as in Ex. 20, but were coated with 1000 Angstroms mass equivalent of Pt, rather than Ni and then Pt. Square pieces of the polyimide supported nanostructured films, 5 cm.sup.2 in area, were placed in each square hole of the masks. The assembly was preheated to 210-215.degree. C., pressed at 14.2 MPa (0.12 tons/cm.sup.2) for one minute, and cooled under pressure. The polyimide substrates supporting the whiskers were peeled away leaving the Pt coated nanostructure in the 5 cm.sup.2 area of the filled membrane. SEM micrographs show the compressed 3-layer MEA to be 31 micrometers thick and demonstrate that the pressing process embedded the nanostructured electrode in the surface of the filled membrane.

Detailed Description Text - DETX (117):

FIG. 7, curve A shows an initial polarization curve of voltage versus current produced by the fuel cell assembly of this example under hydrogen and oxygen pressures of 63 kPa absolute (9 psig) and 327 kPa absolute (18 psig), respectively, a cell temperature of 40.degree. C., and 200 sccm flow rates.

Detailed Description Text - DETX (119):

In Example 22, a three layer MEA was prepared using the same TIPS membrane A membrane partially filled with Nafion, the same type of nanostructured electrodes and the same procedures as described in Example 21. However, prior to attaching nanostructured electrodes, an additional drop of 5 wt % Nafion solution was applied to each area of filled membrane exposed through the 5 cm.sup.2 square holes of the polyimide masks, and dried at 40.degree. C. for 15 minutes. Pt coated electrode were attached as in Ex. 21. In this instance, the Pt coated electrode are embedded into the thin surface layer of solution cast Nafion left on the surface of the filled membrane. Assuming 30 drops per ml, the dried thickness of the cast Nafion layer would be about 3 micrometers. The nanostructure electrode are about 1 to 2 micrometers long and about 30-60 nm wide.

Detailed Description Text - DETX (123):

In Example 23, a 20 wt % solution of p-STSI in a 70/30 v/v mix of MeOH and water was prepared. A 2.5 cm diameter disc of the TIPS membrane A was placed over the holes in the flat bottom of a Coors D37 ceramic funnel inserted in the top of a 250 ml vacuum flask, connected via a rubber hose to a Venturi air device to provide suction. Six drops of the solution were applied to the TIPS disc and air pressure applied to the Venturi device sufficient to pull the solution through the membrane, which process took about 8 seconds. After drying, the disk was about 75 micrometers thick at its center. FIG. 9 is a scanning electron micrograph taken at 1000.times. magnification of the top surface of the membrane. After being partially filled with p-STSI, illustrating a significant degree of open porosity still existing in the membrane.

Detailed Description Text - DETX (124):

Pt coated electrode similar to those described in Example 21 were pressed into the partially filled membrane using 18.9 MPa (0.16 tons/cm.sup.2) pressure at 110.degree. C., by preheating for 1 minute, pressing for 1 minute and cooling under pressure for 4 minutes. FIG. 10 is a cross-sectional scanning electron micrograph taken 1000.times. magnification showing that the

MEA thickness is reduced to 59 micrometers from the initial 89 micrometers. Surprisingly, the membrane now appears to be homogeneous and lacks any indication of the initial porosity. This uniformity is still seen at 10,000.times. magnification, in FIG. 11. FIG. 11 also shows the nanostructured electrode embedded in the surface of the membrane. The fact that the process of embedding the nanostructured electrode to form an MEA has so dramatically changed the morphology of the membrane interior was unexpected. Whereas the TIPS membranes coated from Nafion.TM. solution are observed under SEM to have the ionomer coated onto the fibrils of the porous membrane, it appears that the p-STSI has preferentially filled the pore voids as well as wetting the surface of the pore walls.

Detailed Description Paragraph Table - DETL (1):

TABLE I		Summary of	
increases in g/cm.sup.3 of four different porous membranes filled from Nafion .TM. solution using four different procedures		TIPS	TIPS
membrane A	membrane B	membrane C	Poreflon .TM.
		Multi-Dip and	0.61 (Ex. 1) 0.15 (Ex. 2)
Dry Long Soak	0.29 (Ex. 3) 0.44 (Ex. 4)	Vacuum	0.20 (Ex. 6) 0.31 (Ex. 9)
0.057	0.36 (Ex. 7) (Ex. 10)	0.71 (Ex. 8)	0.301 (Ex. 11) Hydraulic Press
0.35 (Ex. 20)	0.093 0.041 0.22 (Ex. 19)	(Ex. 13)	(Ex. 14)

Detailed Description Paragraph Table - DETL (2):

TABLE II		Summary of	
increases in g/cm.sup.3 of three different porous membranes filled from p-STSI solution using three different procedures		TIPS	TIPS
membrane A	membrane B	membrane C	
		Long	
Soak	0.16 (Ex. 5)	Vacuum	0.15 (Ex. 12) Hydraulic press 0.15 (Ex. 24) 0.041
(Ex. 15)	0.113 (Ex. 17)	0.109 (Ex. 16)	0.17 (Ex. 18)

Claims Text - CLTX (3):

b) providing electrode ; and

Claims Text - CLTX (4):

c) compressing together said partially filled membrane and electrode so as to remove void volume from said partially filled membrane and embed said electrode in said partially filled membrane.

Claims Text - CLTX (5):

2. The method according to claim 1, wherein said electrode are nanostructured elements.

Other Reference Publication - OREF (7):

Kenneth G. Kreider, Michael J. Tarlov, James P. Cline, Sputtered thin film pH, electrodes of platinum, palladium, ruthenium, and iridium Sensprs and Actiatprs B 29 (1995) pp. 167-172.